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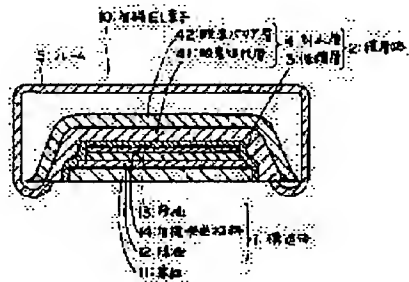
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(54) ORGANIC EL ELEMENT

(57)Abstract:

PURPOSE: To prevent the degradation of a light emitting characteristic caused by oxygen or moisture, and maintain a stable light emitting characteristic over a long period of time by arranging a layer of double layers composed of an oxygen barrier layer and an oxygen absorbing layer as a sealing layer of a layered body.

CONSTITUTION: A sealing layer 4 is arranged outside of a structure body 1 as a layered body 2 through a protective layer 3. This sealing layer 4 is composed of one or more sets of double layers by forming an oxygen absorbing layer 41 and an oxygen barrier layer 42 as a single set. An organic compound, an oxygen absorbing compound, a fluorine compound, metallic fine powder and the like having small ionization potential are used as a material used in the oxygen absorbing layer 41. Metallic oxide, nitride, fluoride and the like used as the protective layer 3 are used as the oxygen barrier layer 42.



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CLAIMS

[Claim(s)]

[Claim 1] The organic EL element characterized by being what has the group of the double layer to which the closure layer of the aforementioned layered product becomes inter-electrode [of the couple-transparent / at least one of these /, or translucent which counters mutually] from an oxygen barrier layer and an oxygen-uptake layer in the organic EL element which has the layered product which consists of the structure which comes to pinch an organic luminescent material and a protective layer arranged in the outside of the structure, and/or a closure layer more than a lot.

[Claim 2] The organic EL element according to claim 1 characterized by carrying out the laminating of an oxygen-uptake layer and the oxygen barrier layer at the electrode side by the side of cathode at this order among the electrodes of the couple to which the group of the double layer which consists of the aforementioned oxygen barrier layer and an oxygen-uptake layer counters aforementioned each other.

[Claim 3] The organic EL element according to claim 1 characterized by being what the aforementioned structure has a substrate, an anode plate, a hole-injection transporting bed, a luminous layer, an electron-injection transporting bed, cathode, a protective layer, and a closure layer in this order, and has the lot of the double layer to which the closure layer has an oxygen-uptake layer and an oxygen barrier layer in this order more than a lot.

[Claim 4] The organic EL element characterized by either [at least] the protective layer of the aforementioned layered product or a closure layer being what contains adsorption, occlusion, or the material to consume for oxygen in the organic EL element which has the layered product which consists of the structure to which at least one of these comes to pinch an organic luminescent material to inter-electrode [of the transparent or translucent couple which counters mutually] and a protective layer arranged in the outside of the structure, and/or a closure layer.

[Claim 5] The organic EL element of the claim 1-3 whose protective layer of the aforementioned layered product is what contains adsorption, occlusion, or the material to consume for oxygen given in any 1 term.

[Claim 6] The organic EL element according to claim 4 or 5 characterized by being what adsorption, occlusion, or the material to consume becomes from one or more matter chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon about the aforementioned oxygen.

[Claim 7] Adsorption, occlusion, or the material to consume the aforementioned oxygen The impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, its oxide, or the impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, or its oxide A magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), The organic EL element according to claim 4 or 5 characterized by making one or more matter chosen from the group which consists of an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon support with 10 or less % of the weight of concentration.

[Claim 8] The organic EL element according to claim 7 characterized by the metal of the fourth aforementioned period of a periodic table being the simple substance of Fe, Co, nickel, Mn, Cr, V, Zn, or Cu, or an alloy more than those kinds.

[Claim 9] The organic EL element according to claim 8 characterized by the alloy of the metal of the fourth aforementioned period of a periodic table being cobalt oxide (II).

[Claim 10] The hydrocarbon in which adsorption, occlusion, or the material to consume has the aforementioned oxygen, and a carbon number has carbon, 3-30, of the first class or the second class The impalpable powder, the thin film, its metal salt, or its oxide of the metal of the fourth period of a periodic table, The impalpable powder of the metal of the fourth period of a periodic table, a thin film, its metal salt, or its oxide Or a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), The thing which one or more matter chosen from the group which consists of an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon was made to support with 10 or less % of the weight of concentration, Or the organic EL element according to claim 4 or 5 characterized by infiltrating activated carbon by 1 or less % of the weight of concentration.

[Claim 11] The organic EL element according to claim 4 or 5 characterized by making one or more matter with which adsorption, occlusion, or the material to consume is chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon in platinum, palladium, a rhodium, ruthenium, or silver support the aforementioned oxygen with 5 or less % of the weight of concentration

[Claim 12] The organic EL element characterized by being that in which the protective layer of the aforementioned layered

product contains a dehydrating agent in the organic EL element which has the layered product which consists of the structure which comes to pinch an organic luminescent material to inter-electrode [of the couple at least with transparent or translucent one of these which counters mutually] and a protective layer arranged in the outside of the structure, and/or a closure layer.

[Claim 13] The organic EL element of the claim 1-11 characterized by being that in which the protective layer of the aforementioned layered product contains a dehydrating agent given in any 1 term.

[Claim 14] The organic EL element according to claim 12 or 13 characterized by the protective layer of the aforementioned layered product being the solid organic substance.

[Claim 15] The organic EL element of the claim 12-14 characterized by being what the aforementioned dehydrating agent becomes from alkali metal or alkaline earth metal given in any 1 term.

[Claim 16] The organic EL element characterized by being what the closure layer of the aforementioned layered product becomes from the light or thermosetting resin containing inorganic composition in the organic EL element which has the layered product which consists of the structure to which at least one of these comes to pinch an organic luminescent material between the electrodes of the transparent or translucent couple which counters mutually and a protective layer arranged in the outside of the structure, and/or a closure layer.

[Claim 17] The organic EL element of the claim 1-15 characterized by being what the closure layer of the aforementioned layered product becomes from the light or thermosetting resin containing inorganic composition given in any 1 term.

[Claim 18] The organic EL element according to claim 16 or 17 characterized by the aforementioned inorganic composition being a silica glass.

[Claim 19] The structure to which at least one of these comes to pinch an organic luminescent material between the electrodes of the transparent or translucent couple which counters mutually, In the organic EL element which has the layered product which consists of the protective layer and/or closure layer which were arranged in the outside of the structure and either [at least] the protective layer of the aforementioned layered product or a closure layer The organic EL element characterized by being what has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg).

[Claim 20] The organic EL element of the claim 1-11 characterized by being that in which the protective layer of the aforementioned layered product has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) given in any 1 term.

[Claim 21] The organic EL element according to claim 4 to 15 characterized by the closure layer of the aforementioned layered product being what has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg).

[Claim 22] The organic EL element of the claim 1-18 characterized by having further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) further on the outside of the closure layer of the aforementioned layered product given in any 1 term.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to organic EL (electroluminescence) element. It continues at the long period of time still more detailed mainly used suitable for the various displays and light emitting device for information industry devices, a stable luminescence property is maintained, and it is related with a long lasting organic EL element.

[0002]

[Description of the Prior Art] The organic EL element consists of the structures which sandwiched an organic luminescent material by the counterelectrode of a couple, from one electrode, an electron is poured in and an electron hole is poured in from the electrode of another side. When this electron and electron hole that were poured in recombine within a luminous layer, luminescence arises. This organic EL element is expected as a full color flat-panel display or a thing replaced with Light Emitting Diode from the height of the shock resistance and visibility, and the versatility of the luminescent color which the organic substance has, and development is furthered.

[0003] It is known that such an organic EL element will fall remarkably compared with the case where the luminescence properties of luminescence brightness, luminous efficiency, and luminescence, such as homogeneity, are the first stages continuation or when it drives during a fixed period discontinuously. As a cause of degradation of such a luminescence property, oxidization of the electrode by moisture, the denaturation of the organic substance, etc. can be cited into the oxidative degradation of the organic material by oxidization of the electrode by the oxygen which invaded in the organic EL element, and generation of heat at the time of a drive, and the air which invaded in the organic EL element. Furthermore, the interface of the structure exfoliates under the influence of oxygen or moisture, or it becomes a trigger that the environment at the time of generation of heat and the drive at the time of a drive was an elevated temperature etc., stress occurs in the interface of the structure by the difference in the coefficient of thermal expansion of each component, and mechanical degradation of the structure of an interface exfoliating can be cited as the cause.

[0004] As invention which prevents degradation of such a luminescence property, the protective coat which becomes the outside surface of the laminated-structure object of ** organic EL element from an electric insulation inorganic compound is prepared. The closure method which prepared the shield layer which consists of matter chosen as the outside of this protective layer from the group which consists of an electric insulation high molecular compound and electric insulation airtight fluids, such as electric insulation glass, an epoxy resin, and silicone resin, (JP,5-89959,A), ** Make packing the thin film EL panel (JP,2-12792,A) with which an insulating material of the shape of a solid-state and gel which has a tooth-back substrate and water absorbent comes to close a thin film EL element, and ** EL element. How to make it share so that 5 oxidization 2 Lynn cannot be touched in it at an EL element (JP,3-261091,A), And sink ** EL element into a fluorocarbon oil, and a dehydrating agent is mixed into the fluorocarbon oil. The closure technology (JP,5-182759,A) using the method (JP,5-41281,A and No. 114486 official report) except moisture and ** photoresist in which moisture resistance is highly airtight etc. is indicated.

[0005]

[Problem(s) to be Solved by the Invention] It is not what the effect of the closure about oxygen can not necessarily be satisfied with the closure method of the aforementioned **] of fully. however, in the thin film EL panel of ** The effect of the closure about oxygen is inadequate too. by the method of ** Since another container with which the EL element was made packing and 5 oxidization 2 Lynn entered into it must be made, in order that 5 oxidization 2 Lynn may react violently with the electrode of an EL element, or the organic substance complicated [production of an element], Since shock resistance must be taken into consideration, are not practical. by the method of ** Since the fluorocarbon oil has the risk of a liquid spill in case it is difficult handling and destruction in the case of closure, since it is a liquid, it is not practical. by the method of ** There was a problem that an element deteriorated as a result broke mechanically, by the difference in the contraction at the time of hardening of such a resin, and the expansion coefficient of an EL element and a closure layer (temperature cycle). It was made in view of the above-mentioned problem, and degradation of the luminescence property by oxygen or moisture is prevented, it continues at a long period of time, a stable luminescence property is maintained, and this invention aims at offering a long lasting organic EL element. Moreover, mechanical degradation of the element by the temperature cycle is prevented, it continues at a long period of time, a stable luminescence property is maintained, and it sets it as other purposes to offer a long lasting organic EL element.

[0006]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, according to this invention, at least one of these to inter-electrode [of the transparent or translucent couple which counters mutually] In the organic EL element which has the

layered product which consists of the structure which comes to pinch an organic luminescent material and a protective layer arranged in the outside of the structure, and/or a closure layer The organic EL element characterized by being what has the group of the double layer which the closure layer of the aforementioned layered product turns into from an oxygen barrier layer and an oxygen-uptake layer more than a lot is offered.

[0007] Moreover, the electrode side by the side of cathode is provided with the organic EL element characterized by carrying out the laminating of an oxygen-uptake layer and the oxygen barrier layer at this order among the electrodes of the couple to which the group of the double layer which consists of the aforementioned oxygen barrier layer and an oxygen-uptake layer counters aforementioned each other.

[0008] Moreover, the organic EL element characterized by being what the aforementioned structure has a substrate, an anode plate, a hole-injection transporting bed, a luminous layer, an electron-injection transporting bed, cathode, a protective layer, and a closure layer in this order, and has the lot of the double layer to which the closure layer has an oxygen-uptake layer and an oxygen barrier layer in this order more than a lot is offered.

[0009] Moreover, in the organic EL element which has the layered product which consists of the structure to which at least one of these comes to pinch an organic luminescent material to inter-electrode [of the transparent or translucent couple which counters mutually] and a protective layer arranged in the outside of the structure, and/or a closure layer, the organic EL element characterized by either [at least] the protective layer of the aforementioned layered product or a closure layer being what contains adsorption, occlusion, or the material to consume for oxygen is offered.

[0010] Moreover, the organic EL element which is that in which the protective layer of the aforementioned layered product contains adsorption, occlusion, or the material to consume for oxygen is offered.

[0011] Moreover, the organic EL element characterized by being what adsorption, occlusion, or the material to consume becomes from one or more matter chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon about the aforementioned oxygen is offered.

[0012] Adsorption, occlusion, or the material to consume the aforementioned oxygen Moreover, the impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, its oxide, or the impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, or its oxide A magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), The organic EL element characterized by making one or more matter chosen from the group which consists of an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon support with 10 or less % of the weight of concentration is offered.

[0013] Moreover, the organic EL element characterized by the metal of the fourth aforementioned period of a periodic table being the simple substance of Fe, Co, nickel, Mn, Cr, V, Zn, or Cu or an alloy more than those kinds is offered.

[0014] Moreover, the organic EL element characterized by the alloy of the metal of the fourth aforementioned period of a periodic table being cobalt oxide (II) is offered.

[0015] Moreover, 3-30, a carbon number the aforementioned oxygen [adsorption, occlusion, or the material to consume] A hydrocarbon with the carbon of the first class or the second class The impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, its oxide, or the impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, or its oxide A magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), The thing which one or more matter chosen from the group which consists of an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon was made to support with 10 or less % of the weight of concentration, or the organic EL element characterized by infiltrating activated carbon by 1 or less % of the weight of concentration is offered.

[0016] Moreover, the organic EL element characterized by making one or more matter with which adsorption, occlusion, or the material to consume is chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon in platinum, palladium, rhodium, a ruthenium, or silver support the aforementioned oxygen with 5 or less % of the weight of concentration be offered

[0017] Moreover, in the organic EL element which has the layered product which consists of the structure which comes to pinch an organic luminescent material to inter-electrode [of the couple at least with transparent or translucent one of these which counters mutually] and a protective layer arranged in the outside of the structure, and/or a closure layer, the organic EL element characterized by being that in which the protective layer of the aforementioned layered product contains a dehydrating agent is offered.

[0018] Moreover, the organic EL element characterized by being that in which the protective layer of the aforementioned layered product contains a dehydrating agent is offered.

[0019] Moreover, the organic EL element characterized by the protective layer of the aforementioned layered product being the solid organic substance is offered.

[0020] Moreover, the organic EL element characterized by being what the aforementioned dehydrating agent becomes from alkali metal or alkaline earth metal is offered.

[0021] Moreover, in the organic EL element which has the layered product which consists of the structure to which at least one of these comes to pinch an organic luminescent material between the electrodes of the transparent or translucent couple which counters mutually and a protective layer arranged in the outside of the structure, and/or a closure layer, the organic EL element characterized by being what the closure layer of the aforementioned layered product becomes from the light or thermosetting resin

containing inorganic composition is offered.

[0022] Moreover, the organic EL element characterized by being what the closure layer of the aforementioned layered product becomes from the light or thermosetting resin containing inorganic composition is offered.

[0023] Moreover, the organic EL element characterized by the aforementioned inorganic composition being a silica glass is offered.

[0024] Moreover, the structure to which at least one of these comes to pinch an organic luminescent material between the electrodes of the transparent or translucent couple which counters mutually, In the organic EL element which has the layered product which consists of the protective layer and/or closure layer which were arranged in the outside of the structure and either at least] the protective layer of the aforementioned layered product or a closure layer The organic EL element characterized by being what has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) is offered.

[0025] Moreover, the organic EL element characterized by being that in which the protective layer of the aforementioned layered product has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) is offered.

[0026] Moreover, the organic EL element characterized by the closure layer of the aforementioned layered product being what has further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) is offered.

[0027] Furthermore, the organic EL element characterized by having further at least the organic layer whose oxygen transmission coefficients are below 1×10^{-12} cc-cm/cm² and S (cmHg) further on the outside of the closure layer of the aforementioned layered product is offered.

[0028] Hereafter, the composition of the organic EL element used for this invention is explained. First, the structure of the organic EL element used for this invention is explained. Especially the composition is not limited and can take arbitrary composition. For example, an anode plate / luminous layer / cathode, an anode plate / hole-injection layer / luminous layer / cathode, an anode plate / luminous layer / electron-injection layer / cathode, or an anode plate / hole-injection layer / luminous layer / electron-injection layer / cathode can be mentioned. Moreover, the layered product of two or more layers is sufficient as each class, and the mixolimnion of two or more material is sufficient as it. These organic substance each class can be formed using the method of heating by the resistance heating method by a boat, a filament, etc. which put in the organic substance proposed by Japanese Patent Application No. No. 028659 [five to], and evaporating, and making deposit the evaporated organic substance on one electrode, and forming an organic layer. Especially the thickness of each class is not limited. The thickness of each class except the electrode of yin and yang is usually 5nm - 5 micrometers. Moreover, material is not limited especially if usually used for an organic EL element. Hereafter, the structure of the organic EL element which consists of an anode plate / hole-injection transporting bed / luminous layer / an electron-injection transporting bed / cathode is explained concretely.

[0029] ** As for the structure of the organic EL element used for a substrate this invention, forming on a substrate is desirable. As for the substrate used for this invention, what has transparency is desirable, and glass, transparent plastics, a quartz, etc. can specifically be mentioned.

[0030] ** It is for acquiring transparency the transparence which consists of an electrode (an anode plate and cathode) of the couple that the electrode used for an electrode this invention has at least transparent one of these or translucent which counters mutually, or to suppose that it is translucent.

** -1 As an anode plate used for an anode plate this invention, what makes electrode material the large (4eV or more) metal, the alloy, the electrical conductivity compounds, and such mixture of a work function can be used suitably. As an example of such electrode material, a transparent material or translucent material with the dielectric, such as metals, such as Au, CuI, ITO and SnO₂, and ZnO, can be mentioned. This anode plate can create these pole matter by making a thin film form by methods, such as vacuum evaporation and sputtering. When taking out luminescence from this electrode, it is desirable to make permeability larger than 10%, and, as for the sheet resistance as an electrode, it is desirable to carry out to below hundreds of ohms / **. Although thickness is furthermore based also on material, 10nm - 1 micrometer can usually be preferably chosen in 10-200nm.

[0031] ** -2 What makes electrode material the small (4eV or less) metal, the alloy, the electrical conductivity compounds, and such mixture of a work function as cathode one side and cathode can be used. As an example of such electrode material, a sodium and sodium-potassium alloy, magnesium, a lithium, magnesium / copper mixture, aluminum/(aluminum 2O₃), an indium, the rare earth metal, etc. can be mentioned. This cathode can create such electrode material by making a thin film form by methods, such as vacuum evaporation and sputtering. Moreover, as for the sheet resistance as an electrode, it is desirable to carry out to below hundreds of ohms / **, and 10nm - 1 micrometer of thickness can usually be preferably chosen in 50-200nm. In addition, in this EL element, it is desirable in order for transparence or supposing that it is translucent to penetrate either this anode plate or cathode, and for the electrode itself to penetrate luminescence and to raise the ejection efficiency of luminescence.

[0032] ** As an organic compound usable as a material of a luminous layer luminous layer, although there is especially no limitation, it can mention fluorescent brighteners, such as a benzothiazole system, a benzimidazole system, and a benzo oxazole system, a metal chelate-ized oxy-NOIDO compound, a styryl benzenoid compound, etc.

[0033] If a compound name is shown concretely, what is indicated by JP,59-194393,A can be mentioned, for example. As the example of representation, it is 2 and 5-screw (5, 7-G t-pentyl-2-benzoxazolyl). - 1, 3, 4-thiadiazole, A 4 and 4'-screw (5, 7-t-pentyl-2-benzoxazolyl) stilbene, 4 and 4' screw [-] [5 and 7-G (2-methyl-2-butyl)-2-benzoxazolyl] stilbene, 2, 5-screw (5, 7-G t-pentyl-2-benzoxazolyl) thiophene, 2, 5-screw [5-alpha and alpha-dimethyl benzyl-2-benzoxazolyl] thiophene, 2, 5-screw [5 and 7-G (2-methyl-2-butyl)-2-benzoxazolyl]-3, 4 diophenyl thiophene, 2, 5-screw (5-methyl-2-benzoxazolyl) thiophene, A 4 and

4'-screw (2-benzoxazolyl) biphenyl, a 5-methyl-2-[2-[4-(5-methyl-2-benzoxazolyl) phenyl] vinyl] benzo oxazole, Benzo oxazole systems, such as 2-[2-(4-chlorophenyl) vinyl] [1 and 2-naphth d] oxazole, 2-2'-(p-phenylenedivinylene)- Benzothiazole systems, such as a screw benzothiazole, Fluorescent brighteners, such as benzimidazole systems, such as 2-[2-[4-(2-benzo imidazolyl) phenyl] vinyl] benzimidazole and 2-[2-(4-carboxyphenyl) vinyl] benzimidazole, can be mentioned. Furthermore, other useful compounds are enumerated by the chemistry OBU synthetic soybeans 1971, 628-637 pages, and 640 pages.

[0034] As the aforementioned chelation oxy-NOIDO compound, what is indicated by JP,63-295695,A, for example can be used. As the example of representation, tris (eight quinolinol) aluminum, screw (eight quinolinol) magnesium, Screw ([BENZO f]-eight quinolinol) zinc, a screw (2-methyl-8-quinolinolato) aluminum oxide, A tris (eight quinolinol) indium, tris (5-methyl-eight quinolinol) aluminum, An eight-quinolinol lithium, a tris (5-chloro-eight quinolinol) gallium, 8-hydroxyquinoline system metal complexes, dilithium EPINTORI dione, etc., such as screw (5-chloro-eight quinolinol) calcium and poly [zinc (II)-screw (8-hydroxy-5-KINORI nonyl) methane], can be mentioned.

[0035] Moreover, as the aforementioned styryl benzenoid compound, what is indicated by the Europe patent No. 0319881 specification and the Europe patent No. 0373582 specification, for example can be used. As the example of representation, 1, 4-screw (2-methyl styryl) benzene, 1, 4-screw (3-methyl styryl) benzene, 1, 4-screw (4-methyl styryl) benzene, JISUCHIRIRU benzene, 1, 4-screw (2-ethyl styryl) benzene, 1, 4-screw (3-ethyl styryl) benzene, 1, 4-screw (2-methyl styryl)-2-methylbenzene, 1, and 4-screw (2-methyl styryl)-2-ethylbenzene etc. can be mentioned.

[0036] Moreover, the JISUCHIRIRU pyrazine derivative currently indicated by JP,2-252793,A can also be used as a material of a luminous layer. As the example of representation, 2, 5-screw (4-methyl styryl) pyrazine, 2, 5-screw (4-ethyl styryl) pyrazine, 2, 5-screw [2-(1-naphthyl) vinyl] pyrazine, 2, 5-screw (4-methoxy styryl) pyrazine, 2, and 5-screw [2-(4-biphenyl) vinyl] pyrazine, 2, and 5-screw [2-(1-pyrenyl) vinyl] pyrazine etc. can be mentioned. As other things, the polyphenyl system compound currently indicated by for example, the Europe patent No. 0387715 specification can also be used as a material of a luminous layer.

[0037] Furthermore, the fluorescent brightener, metal chelate-ized oxy-NOIDO compound which were mentioned above, In addition to a styryl benzenoid compound etc., and [non / for example, / 12-phthaloperi /, (J.Appl.Phys., the 27th volume, L713 (1988))] 1, 4-diphenyl-1,3-butadiene, 1, 1 and 4, and 4-tetrapod phenyl-1,3-butadiene (above Appl. Phys. Lett., the 56th volume, L799 (1990)), A NAFUTARU imide derivative (JP,2-305886,A), a perylene derivative (JP,2-189890,A), An OKISA diazole derivative (JP,2-216791,A or OKISA diazole derivative indicated by Hamada and others at the 38th applied-physics relation union lecture meeting), An aldazine derivative (JP,2-220393,A), a peeler JIRIN derivative (JP,2-220394,A), A cyclopentadiene derivative (JP,2-289675,A), a pyrrolo pyrrole derivative (JP,2-296891,A), A styryl amine derivative (Appl.Phys.Lett., the 56th volume, L799 (1990)), A coumarin system compound (JP,2-191694,A), the international public presentation official report WO 90/13148, Appl.Phys.Lett., vol 58, 18, and P1982 (1991) A high molecular compound which is indicated It can use as a material of a luminous layer.

[0038] It is desirable to use an aromatic JIMECHIRI DIN system compound (thing of the indication to the Europe patent No. 0388768 specification or JP,3-231970,A) as a material of a luminous layer especially in this invention. As an example, a - screw (2 and 2-G t-buthylphenyl vinyl) biphenyl, and 1, 4-phenylene dimethyldiyne, 4, and 4-phenylene dimethyldiyne, 2, 5-xylene JIMECHIRI DIN, 2,6-naphthylenedimethyldiyne, 1,4-biphenylene dimethyldiyne, 1, 4-p-terephylene dimethyldiyne, 9, 10-anthracene G RUJIRU methylidyne, 4, and 4 '4, 4'-screw (2 and 2-diphenyl vinyl) biphenyl etc. can mention those derivatives.

[0039] Thus, although there is especially no limitation about the thickness of the luminous layer formed and it can choose suitably according to a situation, the range of 5nm - 5 micrometers is usually desirable. The luminous layer in an organic EL element offers the place of the reunion of the transportation function, electron, and electron hole to which the charge (an electron and electron hole) which can pour in an electron hole from an anode plate or a hole-injection layer at the time of electric-field impression, and can pour an electron into it from cathode or an electron-injection layer, and which it pouring-functioned and was poured in is moved by the force of electric field, and has the luminescence function to tie this to luminescence etc. In addition, an electron hole is poured in, easy and an electron are poured in and a difference may be between easy. Moreover, although size may be in the transportation function in which it is expressed with an electron hole and the degree of electron transfer, it is desirable to move either at least.

[0040] ** As a material of the hole-injection layer prepared if needed [hole-injection layer], arbitrary things can be chosen and used out of what is commonly used as a hole-injection material of a photo conductor conventionally, or the well-known thing currently used for the hole-injection layer of an organic EL element. The material of a hole-injection layer may have any of pouring of an electron hole, and electronic obstruction nature they are, and either the organic substance or an inorganic substance is OK as it.

[0041] As an example, for example A triazole derivative (references, such as the U.S. JP,3,112,197,B specification), An OKISA diazole derivative (references, such as the U.S. JP,3,189,447,B specification), an imidazole derivative (references, such as JP,37-16096,B) and the poly aryl alkane derivative (the U.S. JP,3,615,402,B specification --) A 3,820,989 specification, a 3,542,544 specification, JP,45-555,B, a 51-10983 official report, JP,51-93224,A, A 55-17105 official report, a 56-4148 official report, a 55-108667 official report, References, such as a 55-156953 official report and a 56-36656 official report, a pyrazoline derivative and a pyrazolone derivative (a U.S. Pat. No. 3,180,729 specification --) A 4,278,746 specification, JP,55-88064,A, A 55-88065 official report, a 49-105537 official report, a 55-51086 official report, A 56-80051 official report, a 56-88141 official report, a 57-45545 official report, References, such as a 54-112637 official report and a 55-74546 official report, a phenylenediamine derivative (a U.S. Pat. No. 3,615,404 specification --) JP,51-10105,B, a 46-3712 official report, a 47-25336 official report, References, such as JP,54-53435,A, a 54-110536 official report, and a 54-119925 official report, an arylamine

derivative (a U.S. Pat. No. 3,567,450 specification and a 3,180,703 specification --) A 3,240,597 specification, a 3,658,520 specification, A 4,232,103 specification, a 4,175,961 specification, A 4,012,376 specification, JP,49-35702,B, A 39-27577 official report, JP,55-144250,A, a 56-119132 official report, References, such as a 56-22437 official report and the West German patent No. 1,110,518 specification, An amino substitution chalcone derivative (references, such as a U.S. Pat. No. 3,526,501 specification), An oxazole derivative (thing of an indication on U.S. Pat. No. 3,257,203 specifications etc.), A styryl anthracene derivative (references, such as JP,56-46234,A), full -- me -- non -- a derivative (references, such as JP,54-110837,A) and a hydrazone derivative (a U.S. Pat. No. 3,717,462 specification --) JP,54-59143,A, a 55-52063 official report, a 55-52064 official report, A 55-46760 official report, a 55-85495 official report, a 57-11350 official report, References, such as a 57-148749 official report and JP,2-311591,A, a stilbene derivative (JP,61-210363,A and a 61-228451 official report --) A 61-14642 official report, a 61-72255 official report, a 62-47646 official report, A 62-36674 official report, a 62-10652 official report, a 62-30255 official report, A 60-93445 official report, a 60-94462 official report, a 60-174749 official report, Reference, silazane derivatives (U.S. Pat. No. 4,950,950 specification), such as a 60-175052 official report, A polysilane system (JP,2-204996,A), an aniline system copolymer (JP,2-282263,A), the conductive polymer oligomer (especially thiophene oligomer) currently indicated by JP,1-211399,A can be mentioned.

[0042] Although the above-mentioned thing can be used as a material of a hole-injection layer A porphyrin compound (thing of the indication to JP,63-2956965,A etc.), an aromatic tertiary-amine compound and a styryl amine compound (a U.S. Pat. No. 4,127,412 specification --) JP,53-27033,A, a 54-58445 official report, a 54-149634 official report, A 54-64299 official report, a 55-79450 official report, a 55-144250 official report, It is desirable references, such as a 56-119132 official report, a 61-295558 official report, a 61-98353 official report, and a 63-295695 official report, and to use especially an aromatic tertiary-amine compound.

[0043] As an example of representation of the above-mentioned porphyrin compound, porphin, 1, 10 and 15, 20-tetrapod phenyl-21H, and 23H-porphin copper (II), 1, 10, 15, 20-tetrapod phenyl-21H, and 23H-porphin zinc (II), A 5, 10, 15, 20-tetrakis (pentafluorophenyl)-21H, and 23H-porphin, A silicon phthalocyanine oxide, aluminum phthalocyanine chloride, A phthalocyanine (non-metal), a dilithium phthalocyanine, a copper tetramethyl phthalocyanine, A copper phthalocyanine, a chromium phthalocyanine, a zinc phthalocyanine, a lead phthalocyanine, a titanium phthalocyanine oxide, Mg phthalocyanine, a copper octamethyl phthalocyanine, etc. can be mentioned.

[0044] moreover, as an example of representation of the aforementioned aromatic tertiary-amine compound and a styryl amine compound N, N, N', the N'-tetrapod phenyl -4, a 4'-diamino phenyl, N, N'-diphenyl - N, N'-screw-(3-methylphenyl)-[1 and 1'-biphenyl]-4, a 4'-diamine, 2 and 2-screw (4-G p-tolylamino phenyl) propane, 1, and 1-screw (4-G p-tolylamino phenyl) cyclohexane, N, N, N', the N'-tetrapod-p-tolyl -4, a 4'-diamino phenyl, A 1 and 1-screw (4-G p-tolylamino phenyl)-4-phenylcyclohexane, A screw (4-dimethylamino-2-methylphenyl) phenylmethane, A screw (4-G p-tolylamino phenyl) phenylmethane, N, N'-diphenyl - N, N'-JI (4-methoxyphenyl) -4, a 4'-diamino biphenyl, N, N, N', the N'-tetrapod phenyl -4, a 4'-diamino phenyl ether, A 4 and 4'-screw (diphenylamino) KUODORI phenyl, N and N, N-TORI (p-tolyl) amine, 4-(G p-tolylamino)-4'-[4 (G p-tolylamino) Styryl] stilbene, 4-N and N-diphenylamino-(2-diphenyl vinyl) benzene, 3-methoxy - 4' - N and N-diphenylamino still benzene, N-phenyl carbazole, etc. can be mentioned. Moreover, the above-mentioned aromatic JIMECHIRI DIN system compound shown as a material of a luminous layer can also be used as a material of a hole-injection layer.

[0045] Although especially the thickness as a hole-injection layer is not restricted, it is usually 5nm - 5 micrometers. This hole-injection layer may be a double layer structure which consists of one sort of the material mentioned above, or two sorts or more and which may be structure much more and consists of two or more layers of the same composition or different-species composition.

[0046] ** As the material, arbitrary things can be chosen and used for the electron-injection layer prepared if needed [electron-injection layer] out of a conventionally well-known compound that what is necessary is just to have the function to transmit the electron poured in from cathode to a luminous layer.

[0047] as an example -- nitration full -- me -- non -- a derivative and JP,57-149259,A -- The anthra quinodimethan derivative currently indicated by the 58-55450 official report, the 63-104061 official report, etc., Polymer Preprints, Japan Vol.37, the diphenyl quinone derivative indicated by the No.3(1988) p.681 grade, Heterocycle tetracarboxylic acid anhydrides, such as a thiopyran dioxide derivative and a naphthalene perylene, A carbodiimide, Japanese Journal of Applied Physics, 27, L 269 (1988), The full ORENIRIDEN methane derivative currently indicated by JP,60-69657,A, the 61-143764 official report, the 61-148159 official report, etc., The anthra quinodimethan derivative and anthrone derivative which are indicated by JP,61-225151,A, the 61-233750 official report, etc., Appl.Phys.Lett., the OKISA diazole derivative indicated by Hamada and others at 55, 15, 1489, or the above-mentioned 38th applied-physics relation union lecture meeting, a series of electron-transport nature compounds currently indicated by JP,59-194393,A are mentioned. In addition, although the aforementioned electron-transport nature compound was indicated as a material of a luminous layer in JP,59-194393,A, according to examination of this invention person, it became clear that it can use also as a material of an electron-injection layer.

[0048] On the metal complex of an eight-quinolinol derivative, and a concrete target, moreover, tris (eight quinolinol) aluminum, Tris (5, 7-dichloro-eight quinolinol) aluminum, tris (5, 7-dibromo-eight quinolinol) aluminum, Tris (2-methyl-eight quinolinol) aluminum, etc. the metal complex which the central metal of these metal complexes placed and replaced with In, Mg, Cu, calcium, Sn, or Pb can be used as a material of an electron-injection layer. In addition, that by which a metal free-lancer, metal phthalocyanines, or those ends are replaced with the alkyl group, the sulfone machine, etc. is also desirable. Moreover, the JISUCHIRIRU pyrazine derivative illustrated as a material of a luminous layer can also be used as a material of an

electron-injection layer.

[0049] Although especially the thickness as an electron-injection layer is not restricted, it is usually 5nm - 5 micrometers. This electron-injection layer may be a double layer structure which consists of one sort of the material mentioned above, or two sorts or more and which may be structure much more and consists of two or more layers of the same composition or different-species composition.

[0050] Next, the layered product (a protective layer and/or closure layer) used for this invention is explained concretely, referring to a drawing for every invention. At the time of production of an organic EL element, a protective layer is used in order to prevent the influence of the mechanical obstacle in the case of electrode-terminal installation and oxygen, and moisture. A closure layer is used in order to prevent the influence of external oxygen and moisture everlastingly.

[0051] 1. The organic EL element of invention of the first invention first is having the closure layer 4 arranged in the outside of the structure 1 through a protective layer 3 as a layered product 2, as shown in drawing 1. This closure layer 4 consists of more than lots of the double layer which made the lot the oxygen-uptake layer 41 and the oxygen barrier layer 42. Hereafter, it explains still more concretely about a protective layer 3 and the closure layer 4.

[0052] 1) Although it is not necessary to necessarily prepare if an injury is not done to the lower structure 1 from the chemical property of the material itself which constitutes the protective-layer closure layer 4, or the physical contact at the time of the laminating, it is desirable to establish the injury on the structure 1 from a viewpoint of pressing down to the minimum. In the desirable mode of the first invention, the protective layer which becomes the outside surface of the structure first mentioned above from an electric insulation inorganic compound is prepared. Although the protective layer should just be prepared on the main front face of a counterelectrode at least, especially its thing established all over the outside surface of the structure is desirable. Moreover, in the organic EL element by which the counterelectrode is prepared in a part of main front face of the layer of either a luminous layer, a hole-injection layer or an electron-injection layer, it is desirable on structure to prepare a protective layer on the main front face of a counterelectrode the portion top in which the counterelectrode is not prepared in the inside on the front face of main of the layer used as the ground of a counterelectrode at least. The electric insulation inorganic compound which is the material of a protective layer That what is necessary is just the thing of the electric insulation which can form membranes by the physical vapor deposition (it may be hereafter called PVD). As an example, MgO, GeO, aluminum 2O3, NiO, CaO, Oxides, such as BaO, Fe 2O3, Y2O3, SiO2, and titanium oxide AlN -- BN -- Si -- three -- N -- four -- Li -- three -- N -- etc. -- a nitride -- SiC -- TiC -- etc. -- carbide -- SrS -- EuS -- CuS -- ZnS -- etc. -- a sulfide -- or -- MgF -- two -- Mg -- (-- OH --) -- two -- BaSO -- four etc. -- various kinds of electric insulation inorganic compounds can be mentioned Especially metal *****, such as GeO, MgO and aluminum 2O3 which can form membranes on comparatively mild conditions, and NiO, are desirable by the reactant vacuum deposition etc. among these electric insulation inorganic compounds.

[0053] The protective layer which consists of an electric insulation inorganic compound can be prepared by the PVD according to the inorganic compound to be used. In making into a luminescence side the side which prepared the protective layer, it chooses material and the formation method so that the protective layer excellent in the translucency to EL light from an organic EL element may be obtained. Although various methods are learned as PVD, it is desirable to apply a vacuum deposition method or a spatter. Although they are subdivisible as follows, for example, it is applicable even if it is which technique.

a. the b. spatters 2, such as a vacuum deposition method resistance heating method, an electron-beam-heating method, a radio frequency heating method, a reactant vacuum deposition, a molecular beam epitaxy method, a hot-wall vacuum deposition, the ion plating method, and the cluster ion beam method, -- very -- a spatter and 2 -- very -- the magnetron-sputtering method and 3 -- very -- reaching -- 4 -- the method [0054] which combined the plasma spatter method, a reactant spatter, the ion beam spatter method, or these very much It is desirable to perform formation of a protective layer so that the organic substance which constitutes the structure which is going to prepare a protective layer may not denaturalize. Although the conditions for the organic substance not denaturalizing change with properties, such as the kind and thermal resistance which the organic substance has, if it puts in another way, it is desirable to keep the temperature of the organic substance general at 200 degrees C or less, and it is desirable to keep at 100 more degrees C or less. Of course, it is not this limitation when a material strong against heat is used like a high molecular compound as the organic substance of business, such as a luminous layer. Below, desirable formation conditions are described according to a method.

** The methods that it is desirable also in ***** are a reactant vacuum deposition and an electron-beam-evaporation method, for example, when the case where the protective coat which consists of a metallic oxide (MgO) by the reactant vacuum deposition is formed is taken for an example, vacuum evaporatio time has 1 or less preferably good hour for 2 or less hours. 20 or less minutes is still more preferably good. Especially the degree of vacuum in the vacuum chamber before vacuum evaporatio has 6×10^{-3} or less desirable Pa, in the stage which introduced oxygen and/or the steam in the vacuum chamber after that, sets preferably 7×10^{-3} or more Pa of pressures in a vacuum chamber to 1×10^{-2} or more Pa, and heats and carries out the vacuum evaporatio of the 1×10^{-2} or less Pa of the metals Mg which are a vacuum evaporatio raw material to 1000 degrees C or less after this. Especially an evaporation rate has a desirable second in 3nm /or less a second 10nm /or less.

** Generally the spatter method spatter has energy higher than a vacuum deposition method in order to calculate the matter to make it deposit from a target with ion. Therefore, conditions are severer than a vacuum deposition method. Especially a desirable method is the reactant spatter method ion beam spatter method in a spatter. When the case (sputtering of the metal Mg is carried out, and it oxidizes by the ion beam of oxygen) where the protective coat which consists of MgO by the reactant ion beam spatter method is formed is taken for an example, vacuum evaporatio time has 10 or less still more preferably good minutes 30 or less minutes preferably for 1 or less hour. Moreover, as for especially the acceleration voltage of oxygen ion, less than [600V] is desirable below 1200V, and especially the beam current has desirable 60mA or less 500mA or less.

[0055] the thickness of the protective layer formed as mentioned above -- an evaporation rate and vacuum evaporation time -- it serves, and it suits, and is come out and decided Although a protective layer can expect the effect so that it is thick, in order to prepare a thick protective layer, vacuum evaporation time must be lengthened, or an evaporation rate must be carried out early, and the damage of the organic substance in the structure also becomes large in connection with this. Therefore, an upper limit is needed also for the thickness of a protective layer. For example, since the damage which the organic substance receives is serious when forming MgO by the reactant vacuum deposition, and membranes are formed by the highest evaporation rate (10nm/(second)), it is necessary to carry out vacuum evaporation time in this case in 20 or less minutes. And the upper limit of the thickness at this time is about 12 micrometers. On the other hand, the minimum of the thickness of a protective layer is decided by existence of the protective effect, generally, by less than about 10nm, is too thin and cannot fully demonstrate the function as a protective layer. In addition, it is desirable to inhibit property degradation of the luminous layer in the morphosis of a protective layer and a counterelectrode as much as possible from [in obtaining a long lasting organic EL element], and it is desirable for that to form a protective layer under vacuum environment. And since it is the same, especially the thing for which from formation of the luminous layer which constitutes the structure to formation of a protective layer is performed under a series of vacuum environment is desirable.

[0056] Moreover, in this invention, an electric insulation macromolecule can be suitably used as other materials of a protective layer. Although this electric insulation high molecular compound should be just meltable to fluorine system solvents, such as what can form membranes by the physical vapor deposition (it may be hereafter called PVD), a thing which can form membranes by chemistry gaseous-phase contact printing (it may be hereafter called CVD) or perfluoro alcohol, the perfluoro ether, and a perfluoro amine, especially the small thing of a moisture vapor transmission is desirable. As an example of each electric insulation high molecular compound, the following can be mentioned, respectively.

[0057] ** The electric insulation high-molecular-compound polyethylene which can form membranes by PVD, polypropylene, polystyrene, a polymethylmethacrylate, a polyimide (that to which two kinds of monomers were made to deposit on a substrate, and carried out the polymerization.) A technical journal, 1988 and 30, 22 references, a polyurea (that to which two kinds of monomers were made to deposit on a substrate, and carried out the polymerization.) The copolymer of a technical journal, 1988 and 30, 22 references, the fluorine system high molecular compound currently indicated by JP,63-18964,A, the fluorine system high molecular compound currently indicated by JP,63-22206,A, the fluorine system high molecular compound currently indicated by JP,63-238115,A, a polytetrafluoroethylene, a polychlorotrifluoroethylene resin, poly dichlorodifluoroethene, a chlorotrifluoroethylene, and dichlorodifluoroethene, the fluorine-containing copolymer which has a cyclic structure (refer to Japanese-Patent-Application-No. No. 129852 [three to] official report).

[0058] ** The electric insulation high-molecular-compound polyethylene which can form membranes by CVD [a plasma polymerization method (plasma CVD)], a polytetrafluoroethylene, a polyvinyl trimethyl silane, poly methyl trimetoxysilane, a polysiloxane, etc.

[0059] ** The fluorine system high molecular compound currently indicated by the electric insulation high-molecular-compound Provisional-Publication-No. No. 18964 [63 to] official report meltable to fluorine system solvents, such as perfluoro alcohol, the perfluoro ether, and a perfluoro amine The fluorine system high molecular compound currently indicated by JP,63-22206,A, The fluorine system high molecular compound currently indicated by JP,63-238115,A, Fluorine system high molecular compounds, such as a copolymer of a polychlorotrifluoroethylene resin, poly dichlorodifluoroethene, a chlorotrifluoroethylene, and dichlorodifluoroethene, and a fluorine-containing copolymer (refer to Japanese-Patent-Application-No. No. 129852 [three to] official report) which has a cyclic structure.

[0060] A protective layer can be prepared according to the high molecular compound to be used by PVD (high molecular compound of the above-mentioned **), CVD (high molecular compound of the above-mentioned **), the cast method, or the spin coat method (high molecular compound of the above-mentioned **), respectively. Although the thickness of the protective layer in this case is based also on the material and the formation method of using, it is desirable that it is 10nm - 100 micrometers.

Moreover, in making into a luminescence side the side which prepared the protective layer, it chooses material and the formation method so that the protective layer excellent in the translucency to EL light from an organic EL element may be obtained.

Formation of the protective layer by the all directions method can be performed as follows, for example.

- PVD can use the same method as the case of an inorganic electric insulation macromolecule. Although membrane formation conditions change with a raw material and kinds of PVD to apply For example, in the case of a vacuum deposition method (a resistance heating method, an electron-beam-heating method, radio frequency heating method) In general 1×10^{-2} or less Pa of degree of vacuums before vacuum evaporation preferably 6×10^{-3} or less Pa, The heating temperature of the source of vacuum evaporation is 600 degrees C or less, substrate temperature is 100 degrees C or less preferably [200 degrees C or less] in general, and it is preferably [in general / 700 degrees C or less] desirable to form an evaporation rate as 3nm/second or less preferably [second] 50nm/or less.

[0061] - The plasma polymerization which carries out the polymerization of the monomer of gases, such as CVD ethylene and a propylene, by plasma is desirable. Since substrate temperature becomes an elevated temperature, the general pyrolysis CVD is unsuitable.

[0062] - Dissolve the cast method raw material in fluorine system solvents, such as perfluoro alcohol, the perfluoro ether, or a perfluoro amine, and obtain a protective layer by making it air-dry for 8 to 16 hours after developing this solvent to the structure. Although ***** in between, whenever it may make it dry exceeding 16 hours if the drying time is 8 hours or more, since the big difference to the grade of dryness does not come out, it is unsuitable. About **** 12 hour is suitable for the drying time. The concentration of the raw material in a solution is suitably chosen according to the thickness of the protective layer made into the

purpose.

[0063] - Obtain a protective layer by making it dry like the case of the cast method after carrying out suitable amount dropping on the structure which is rotating preferably the solution obtained like the case of the spin coat method above-mentioned cast method by 200 - 8000rpm 100 to 20000 rpm and rotating this structure for 10 to 30 seconds preferably for further 5 to 60 seconds as it is. Although the drip of the solution at this time changes with sizes of the structure or the organic EL element which it is going to close, it is 0.5-3ml preferably 0.6-6ml in the usual structure or the usual organic EL element of a size (25x75x1.1mm) of slide glass. although the concentration of the raw material in a solution is suitably chosen like the case of the cast method according to the thickness of the protective layer made into the purpose -- the range -- the case of the cast method -- narrow -- 1-40 from points, such as control of thickness, and membranous homogeneity, -- g/100ml is 4-20g / 100ml preferably

[0064] In addition, also in which method of the cast method and the spin coat method, a vacuum dryer etc. is used after air-drying, 30-100 degrees C, it is 50-80 degrees C preferably, and drying further is preferably desirable for 8 to 16 hours for 1 to 24 hours.

[0065] 2) Closure layer ** composition : carry out the laminating of the group of a double layer which has the oxygen-uptake layer 41 and the oxygen barrier layer 42 from the nearer one in the cathode 13 side of the structure 1 at this order more than a lot on the aforementioned protective layer 3.

** Thickness : a number - 100 micrometers of numbers have a desirable lot.

** The laminating method : it is desirable to adopt the laminating method of suppressing damage on the structure at the time of a laminating as much as possible. The same laminating method as a protective layer can be used. Dip coating, the spin coating method, etc. which are learned as the method of application of a macromolecule can be used for others.

Oxygen-uptake layer : ** As a material used for the oxygen-uptake layer 41 (i) The small organic compound of ionization POTENSHARUI, for example, electron hole transportation material of an electrophotography photo conductor, (ii) oxygen adsorptivity compounds, such as an amine system compound and a hydrazone compound, (iii) small metals of a work function, such as Fe, Co, nickel and Cu whose (iv) metal impalpable powder, for example, particle size, is about several micrometers, and alkali metal, such as a fluorine system compound, for example, the inactive liquid of fluorine carbonizing-ized hydrogen etc., and a rare earth metal, -- for example aluminum, In, Mg, Yb, Zr, Na, K, etc. can be mentioned. As a form of the absorption layer of oxygen, the distributed films (a butyral resin, PC, PS, etc.) to the solid-state liquids (the vacuum evaporation film, spatter film, etc.) or macromolecule of the simple substance of the above-mentioned matter can be mentioned.

** As an oxygen barrier layer oxygen barrier layer, polyamide system resins, such as the metallic oxide and nitride which were used as a protective layer, a fluoride and the matter with which it is known that an oxygen transmission coefficient is small, for example, polyvinyl alcohol, isobutylene isoprene rubber, polyethylene, the poly nitril system resin, a polyvinylidene chloride (saran), and nylon 6, etc. can mention Si system nitride well-known as a PASSHUBESHON film of a semiconductor device etc. As a form of an oxygen barrier layer, the vacuum evaporation film of the above-mentioned matter, a spatter film, a macromolecule application film, etc. can be mentioned.

** Still more in addition to this, you may form a frame 5 in the outside of this closure layer 4 with glass or a resin further if needed.

[0066] 2. The organic EL element of invention of the second invention second is characterized by either [at least] the protective layer 3 of a layered product 2 or the closure layer 4 containing adsorption, occlusion, or the material 6 to consume for oxygen, as shown in drawing 2 . In this second invention, it is not necessary to carry out strict distinction with a protective layer and a closure layer. Moreover, you may prepare only one side. In addition, when a solid is used as a closure layer, as for a glue line 7, it is desirable to use it in order to perform closure with a substrate more powerfully. You may make a closure layer use also [glue line]. making adsorption, occlusion, or the material to consume contain oxygen in either these protective layers and a closure layer (henceforth protection closure layer 2') -- the oxygen inside the element of a minute amount -- adsorption and occlusion -- or it is made to consume and the influence of the oxygen to an electrode or an organic material is prevented You may make the matter with which adsorption etc. carries out oxygen into a glue line contain. As the adsorption method of oxygen, any of physical adsorption and chemical absorption are sufficient. In addition, it can say that oxygen is taken in physically [the occlusion of oxygen], or chemically, and an inclusion, an intercalation, and adsorption can be mentioned as the method, for example.

Consumption of ***** can mean consumption of the oxygen by the chemical reaction, and can mention oxygen and coordination, such as hydroxylation, peroxidation, and hydration, as the method, for example. As a form of a protection closure layer, if a substrate and the structure can be covered, there will be especially no limit. When a protection closure layer consists of a metal tabular object, a metal thin film, the film made of a resin, resin mold goods, and glassware, an oxygen adsorbent etc. may be applied, or it may ***** and you may make it apply or deposit. Moreover, when two, a protective layer and a closure layer, are distinguished and prepared, you may insert between them. Moreover, when a protection closure layer consists of a gel, a letter of half-kneading, and liquefied matter, an oxygen adsorbent etc. can be kneaded and it can be used dispersedly. Moreover, when producing a protection closure layer using thermosetting resin, a photoresist, or a reactant resin, an oxygen adsorbent etc. can be kneaded in a raw material and can be dispersedly used for it. Although various adhesives can be used when pasting up a protection closure layer on a substrate, you may knead and use an oxygen adsorbent etc. into adhesives. As for contents, such as an oxygen adsorbent, it is desirable that it is 10 or less % of the weight among a protection closure layer. When it exceeds 10 % of the weight, the homogeneity of a protection closure layer may be spoiled. 0.01 - 5% is still more desirable.

[0067] As adsorption, occlusion, or a material to consume, the following matter can be mentioned for oxygen, for example.

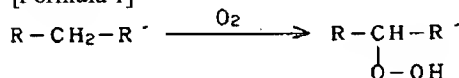
** What consists of one or more matter chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a

silica alumina, a zeolite, a silica, a zirconia, and activated carbon (what was calcinated at the temperature of 120 degrees C or more among inert gas is desirable.) [0068] ** The impalpable powder of the metal (Fe, Co, nickel, Mn, Cr, V, Zn, Cu) of the fourth period of a periodic table, A thin film, its metal salt, its oxide, or the metal of the fourth period of a periodic table (Fe, Co, nickel, Mn, Cr, V, Zn, Cu), The metal salt or its oxide A magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), An activated alumina, a silica alumina, a zeolite, a silica, a zirconia, activated carbon (what was calcinated at the temperature of 120 degrees C or more among inert gas is desirable.) from -- 5% or less of the concentration which was supported to what consists of one or more matter chosen from the becoming group and which carries out matter support is still more desirable preferably [10 or less % of the weight] For example, a cobalt oxide (II) CoO crystal can be mentioned. This matter reacts by oxygen and the following reaction formulae with the crystalline compound which adsorbs oxygen.

$\text{CoO} + 1/4 \text{O}_2 \rightarrow 1/2 \text{Co}_2\text{O}_3$ [0069] ** the hydrocarbon in which a carbon number has carbon of the first class of 3-30, or the second class -- for example An alkyl cyclohexane, an alkane, an alkene, a cumene, etc. The impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, its oxide, or the impalpable powder of the metal of the fourth period of a periodic table, A thin film, its metal salt, or its oxide A magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), The thing which one or more matter chosen from the group which consists of an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon was made to support with 10 or less % of the weight of concentration, or matter into which activated carbon was infiltrated by 1 or less % of the weight of concentration [0070] ** It is the matter [0071] which made one or more matter chosen from the group which consists of a magnesium oxide, a magnesium carbonate, an iron oxide, titanium oxide, a bentonite, the acid clay, a montmorillonite, the diatom earth (clay mineral), an activated alumina, a silica alumina, a zeolite, a silica, a zirconia, and activated carbon support platinum, palladium, a rhodium, RUCHINIUMU, or silver with 5 or less (still more preferably 0.001 % of the weight or more less than per % of the weight) % of the weight of concentration preferably. The reason for the ability to use such matter suitably in this invention is explained below. ** a case -- the compound with a large surface area -- oxygen and an organic substance molecule -- adsorbing -- capacity -- it is . ** a case -- the metal itself and oxygen -- oxidizing -- having -- things -- oxygen -- consuming . Moreover, a metal, a metal salt, and a metallic oxide have the capacity to adsorb oxygen. In the case of cobalt oxide (II), the reaction for which a crystal absorbs oxygen and turns into another crystal is used. ** a case -- an alkane and an alkene -- consume oxygen by the reaction as a metal shown a catalysis by existence and shown in the following formula by it In the case of the metal supported by especially the inorganic substance, since these products also adsorb oxygen and do not take out oxygen out of a system, it excels.

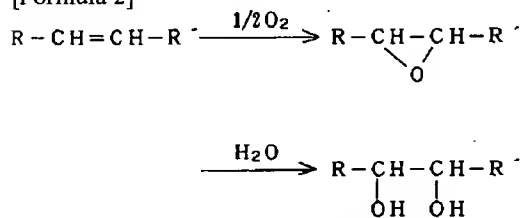
[0072]

[Formula 1]



[0073]

[Formula 2]



[0074] ** a case -- the same capacity as ** and ** -- it is . When especially activated carbon is used for support, it is effective from the size of the surface area. Moreover, the reaction of $1/2 \text{O}_2 + \text{C} \rightarrow \text{CO}$ also occurs, and a carbon monoxide is adsorbed into activated carbon as it is.

[0075] 3. The protective layer used for the third invention invention of the third contains a dehydrating agent 31, as shown in drawing 3 . As a base material of the protective layer 3 used for the third invention, if it is a solid thing at a room temperature, there is especially no limit, for example, it can use an inorganic substance like metal membranes, such as polymer, such as a polyolefine, a polyether, a polycarbonate, and a polyamide, the Du Pont make, the organic substance of the shape of amorphous like tradename: Teflon AF], aluminum, and lead, or alpha-Si:alpha-SiC, alpha-C, and GeO. Especially Teflon AF is desirable especially. Moreover, as a method of producing a protective layer, although there is especially no limit, for example, it can mention the applying method, a vacuum deposition, the spin coat method, sputtering, CVD, etc., since an organic luminescent material is weak with heat, the spin coat method is desirable [a limit]. As a dehydrating agent 31 made to contain in a protective layer, although the anhydrides (sulfuric-anhydride magnesium, anhydrous sodium sulfate, etc.) of a salt, chloride (calcium chloride, lithium chloride, etc.) oxides (calcium oxide etc.), silica gel, a zeolite, a molecular sieve, activated carbon, graphite, etc. can be used for example, alkali metal or especially alkaline earth metal (sodium, a potassium, calcium, magnesium, etc.) are desirable. The content of a dehydrating agent is 10 or less % of the weight among a protective layer. The dehydrating agent of the amount exceeding 10 % of the weight may destabilize a protective layer. In addition, you may prepare a closure layer etc. in the outside of the protective layer 3 containing a dehydrating agent 31 further.

[0076] 4. The closure layer used for the fourth invention consists of the light or the thermosetting resin layer 43 containing inorganic composition 44, as shown in drawing 4. Moreover, you may carry out the laminating of other closure layers on this closure layer 4 if needed. Moreover, you may prepare a protective layer in this closure layer 4 bottom. A metal particle, an inorganic-oxide particle, etc. can be mentioned as inorganic composition 44. Specifically, particles, such as an alumina, a silica glass, colloidal silica, borosilicate glass, beta-eucryptite, barium glass, CHITSU-ized silicon, CHITSU-ized beryllium, and silicon carbide, can be mentioned. As for such inorganic composition, it is desirable that it is 95 or less % of the weight of a 50-% of the weight or more composition ratio to all closure layers, and it is still more desirable that it is 85 or less % of the weight of a 60-% of the weight or more composition ratio. As for especially a limit, as a photoresist, what there is not and consists of a polyfunctional monomer, a photopolymerization initiator (photosensitizer), a reduction agent, a polymerization inhibitor, etc. at least as composition before hardening is desirable. As a wavelength region of light, although there is especially no limit, it is desirable preferably to contain the component which reacts in a light field (380-650nm). By controlling the closure layer 4 by the above-mentioned composition, a uniform film can be formed, the contraction and coefficient of thermal expansion at the time of hardening (polymerization) of a closure layer can be controlled, and degradation accompanying the stress given to an element can be suppressed. As mentioned above, you may carry out the laminating of other closure layers on the closure layer 4 which consists of a photoresist layer 43 containing such inorganic composition 44. As other closure layers, an oxygen barrier layer, a hydrophobic layer, an oxygen adsorption layer, a moisture absorption layer, etc. can be mentioned, for example. Moreover, before hardening, since the above-mentioned light or thermosetting resin is a fluidity, it can change and harden the configuration of a back side according to the situation of installing an organic EL element. For this reason, when carrying out the laminating of other above-mentioned closure layers, the film which has the material which can be solidified by having a fluidity in early stages and performing suitable processing, and flexibility is desirable. As such a photoresist or thermosetting resin, an isobutylene-isoprene-rubber system resin, a styrene-butadiene-rubber system resin, a chloroprene system resin, an acrylic resin, an epoxy resin, a fluorine system resin, a silicone system resin, etc. can be illustrated, for example. Furthermore, as for the above-mentioned material, it is desirable that it is what is excellent in electric insulation and does not have generating of a by-product in the case of hardening, and an epoxy system resin and its silicone system resin are desirable especially from this.

[0077] 5. The layered product used for the fifth invention consists of what formed further at least the organic layer 22 whose oxygen transmission coefficients are 1×10^{-12} cc-cm/cm², s, and (cmHg) the following, as shown in drawing 5. It is desirable to carry out the laminating of the further waterproof closure layer to this organic layer 22 top or the bottom.

Moreover, you may prepare a protective layer in this organic layer 22 bottom. You may be the composition shown in drawing 6 and drawing 7 other than the example shown in drawing 5. As a measuring method of an oxygen transmission coefficient, the method indicated by volume [of polymer chemistry / 16th] No. 168 (1959), the method indicated by J.Polym.Sci.part2A-2 vol.8 p.467 (1970) can be mentioned, for example. As a concrete material, thin films, such as poly vinylidene chloride (trade name : saran), a polyvinyl chloride, polyvinyl alcohol, a cellulose, cellographane, and acetic-acid fiber, can be mentioned. As the forming-membranes method, there is especially no limit and it can use a vacuum deposition, a polymerization method, a spatter, the cast method, the spin coat method, etc. In addition, you may be the method of carrying out thermocompression bonding of the film which consists of the above-mentioned material as the other methods. Furthermore, when using a wet method (for example, the cast method, the spin coat method), it is desirable to carry out the formation epigenesis film of the closure layer of waterproof chemical resistance beforehand. As mentioned above, although explained for every invention, you may combine suitably invention from the first to the fifth.

[0078]

[Example] Hereafter, an example explains this invention still more concretely.

[Example 1]

Using the glass plate (white-board glass by Hoya Corp.) of the size of 25x75x1.1mm of production of the structure of an organic EL element as a substrate, on this substrate, the ITO film was formed by the thickness of 100nm, and it considered as the transparent electrode (the substrate by which the ITO film was formed is hereafter called transparent support substrate). After pure water's washing for 5 minutes after cleaning this transparent support substrate ultrasonically for 30 minutes by isopropyl alcohol, and carrying out a rinse by isopropyl alcohol after that, it is dryness N₂. Gas was sprayed and it was made to dry. Finally it washed for 10 minutes by photochemical cleaner or cleaning equipment (SAMUKO international company make). The transparent support substrate after washing is fixed to the substrate electrode holder of a commercial vacuum evaporation system (Japanese vacuum-technology company make). They are N and N'-diphenyl to the resistance heating boat made from molybdenum. - N, N'-screw-(3-methylphenyl)-[1 and 1'-biphenyl]-4, a 4'-diamine It put in (it having been hereafter called TPD), and 200mg (henceforth Alq.) of tris (eight quinolinol) aluminum was put into the different resistance heating boat made from molybdenum, and the inside of a vacuum game par was decompressed up to 1×10^{-4} to 4 Pa. [200mg]

[0079] Subsequently, heated the aforementioned resistance heating boat into which TPD was put to 215-220 degrees C, TPD was made to deposit on the ITO film of a transparent support substrate in a 0.1-0.3nm [/second] evaporation rate, and the hole-injection layer of 60nm of thickness was formed. The substrate temperature at this time was a room temperature. Subsequently, heated the resistance heating boat made from molybdenum into which Alq. was put to 275 degrees C, fixing to a substrate electrode holder the transparent support substrate by which the hole-injection layer was formed, Alq. was made to deposit on a hole-injection layer in a 0.1-0.2nm [/second] evaporation rate, and the luminous layer of 60nm of thickness was formed. The substrate temperature at this time was also a room temperature. Next, the resistance heating boat made from molybdenum into which (Magnesium Mg) 1g was put beforehand, and the resistance heating boat made from molybdenum into which (Silver Ag) 500mg was put beforehand are heated, respectively, the vacuum evaporation of Mg was carried out by the

1.6nm [/second] evaporation rate, the vacuum evaporation of Ag was simultaneously carried out by the 0.1nm [/second] evaporation rate, and the electrode (counterelectrode) of 160nm of thickness which consists of a mixed metal of Mg and Ag was prepared on the luminous layer. The organic EL element was obtained by having prepared the ITO film (electrode), the hole-injection layer, the luminous layer, and the counterelectrode on the glass substrate. In addition, in this structure, the laminated-structure object is formed of the ITO film prepared on the glass substrate, the hole-injection layer, the luminous layer, and the correspondence electrode. Here, lead wire was taken out from the Mg:Ag side which is not on ITO and ITO by In sticking by pressure. In this state, once again, it returned to the vacuum tub and decompressed up to 1×10^{-4} Pa.

[0080] Oxygen was introduced in the formation vacuum game par of a protective layer, and the pressure in a vacuum game par was set to 8×10^{-3} Pa. Subsequently, heated the resistance heating boat made from molybdenum containing Mg (thing at the time of counterelectrode production) at 485 degrees C, while carrying out the vacuum evaporation of Mg by the 0.5nm [/second] evaporation rate, it was made to react with the oxygen in a vacuum game par, and the MgO film (protective layer) of 0.3 micrometers (300nm) of thickness was prepared in the outside surface of a laminated-structure object.

[0081] It decompressed up to 1×10^{-4} Pa again after that [of an oxygen adsorption layer and an oxygen barrier layer / formation], and Mg was deposited as a 0.5-micrometer oxygen adsorption layer by the 1nm [/second] evaporation rate. 0.5-micrometer laminating membrane formation of the above MgO was again carried out as an oxygen barrier layer by the same method after that. The element was made to emit light after a laminating to the above and a closure layer.

----- voltage (V) Current density (mA/cm²) Brightness (cd/m²) Luminous efficiency (lm/w)
----- 6 10.3 290 Only five pieces were found but the number of the points emitting [-less] light was [in / the 10 times as many expansion image as this / in 1.47-----, in addition a luminescence side (0.3cm²)] luminescence with quite good homogeneity. From the result of the example 1 of comparison mentioned later, the laminating of a protective layer and a closure layer showed that luminescent ability and luminescence homogeneity were not spoiled.

[0082] On MgO (oxygen barrier layer) of the [example 2] example 1, the laminating of Mg and the MgO was further carried out by the same thickness by the same method as second repetition unit. The element performance after a closure end was almost the same as that of an example 1 as follows.

----- voltage (V) Current density (mA/cm²) Brightness (cd/m²) Luminous efficiency (lm/w) The number of the points emitting [-less] light ----- 6 10.0 270 1.45 Seven piece

-----* It is observation [0083] with a 10 times as many expansion image as this like an example 1 below. 100-micrometer laminating of the Fe impalpable-powder distribution film to the poly car board resin (Pc) was carried out in the following procedures instead of Mg of the oxygen-uptake layer of the [example 3] example 1. The mean particle diameter of Fe is 5 micrometers, distributed concentration is Pc:Fe=50:30 % of the weight conditions, and it is CH₂ Cl₂. Membranes were formed by the dip painting cloth method from the solution. Next, as an oxygen barrier layer, among the vacuum of 1×10^{-2} Pa, the high density polyethylene (Idemitsu petrochemical company make, tradename:440M) was taught to the alumina crucible, and carried out 10-micrometer laminating by the vacuum deposition method (crucible temperature : 370 degrees C). The element performance after a closure end was as follows, and was the same as that of examples 1 and 2.

----- voltage (V) Current density (mA/cm²) Brightness (cd/m²) Luminous efficiency (lm/w) The number of the points emitting [-less] light ----- 6 10.5 287 1.43 Eight piece

----- [0084] The organic EL element was produced like the example 1 except having not prepared the [example 1 of comparison] protective layer, and a closure layer (an oxygen-uptake layer and oxygen barrier layer). The element performance was as follows.

----- voltage (V) Current density (mA/cm²) Brightness (cd/m²) Luminous efficiency (lm/w) The number of the points emitting [-less] light ----- 6 10.6 304 1.50 Three piece

----- [0085] The element was produced like the example 1 except having carried out the laminating only of the [example 2 of comparison] protective layer. Luminescent ability was the same as that of the example 1 of comparison almost.

----- voltage (V) Current density (mA/cm²) Brightness (cd/m²) Luminous efficiency (lm/w) The number of the points emitting [-less] light ----- 6 10.5 300 1.50 Four piece

----- [0086] A homogeneous change of a luminescence side was observed by constant-current continuation drive at the room temperature (23 degrees C) after the check element production end of dark-spot depressor effect, and among the atmosphere. The number of the points emitting [1000 hours after / element production /-less] light was as follows. Measurement was performed with the expansion visual field of being 10 times many as this, like the example and the example of comparison. In addition, the number in a parenthesis shows the number which increased from the early value.

----- example 1 Example 2 Example 3 Example 1 of comparison example of comparison 2
----- -- 10 (5) 11 (4) 9 (1) 105 (92) 70 (66)

It turns out that generating of the point emitting [-less] light is effectively suppressed by -----, consequently the closure layer which is alike and consists of an oxygen-uptake layer and an oxygen barrier layer more.

[0087] It is initial 100 cd/m³ at the inside of the check atmosphere of brightness fall depressor effect, and a room temperature (23 degrees C). From brightness, change of brightness was measured by constant-current continuation drive.

----- half line (time) of brightness **** time (time) of an element ----- The example 1 4,600 15,000 An example 2 9,300 20,000 An example 3 7,500 17,000 The example 1 of comparison 212 953 Example 2 of comparison 508 The closure layer which consists of a 12,000 ----- oxygen-uptake layer and an oxygen barrier layer showed that the fall of brightness was suppressed effectively.

[0088] [Example 4]

What formed the ITO electrode by the thickness of 100nm in the shape of [of the production 25mmx75mmx1.1mm size of the structure of an organic EL element] a glass substrate was used as the transparent support substrate. After cleaning this ultrasonically for 30 minutes by isopropyl alcohol, pure water washed for 30 minutes and prolonged sound wave washing was again carried out for 30 minutes by isopropyl alcohol at the last. And this transparent support substrate is fixed to the substrate electrode holder of a commercial vacuum evaporation system (Japanese vacuum-technology company make). They are N and N'-diphenyl to the resistance heating boat made from molybdenum. - N, N'-screw-(3-methylphenyl)-[1 and 1'-biphenyl]-4, and 200mg (TPD) of 4'-diamines are put in. Moreover, 200mg (Alq.) of tris (eight quinolinol) aluminum was put into the different resistance heating boat made from molybdenum, and the inside of a vacuum chamber was decompressed up to 1×10^{-4} Pa. Heated even the 215-220 degrees C even of the aforementioned boats containing TPD after that, TPD was made to deposit on a substrate in a 0.1-0.3nm [second] evaporation rate, and the hole-injection layer of 60nm of thickness was formed. The substrate temperature at this time was a room temperature. On the hole-injection layer, 60nm laminating deposition was carried out from another boat, having used Alq. as the luminous layer, without taking this out from a vacuum layer. As for vacuum evaporation conditions, boat temperature was [the evaporation rate of 0.1-0.2nm and substrate temperature] a room temperature at 275 degrees C. Next, magnesium 1g was put into the resistance heating boat made from molybdenum, and indium 500mg was put into another resistance heating boat made from molybdenum. The vacuum layer was decompressed up to 2×10^{-4} Pa after that, the indium was evaporated in the 0.03-0.08nm [second] evaporation rate, and magnesium was simultaneously deposited by the 1.7-2.8nm [second] evaporation rate from another boat made from molybdenum by the resistance heating method. The boat temperature of magnesium and an indium was 500 degrees C and about 800 degrees C, respectively. The above condition, 150nm laminating vacuum evaporation of the mixed metal electrode of magnesium and an indium was carried out, and it was used as the counterelectrode on the luminous layer. The structure of the organic EL element of the element composition of ITO/TPD/Alq/Mg:In was made. The initial performance of this organic EL element is voltage 7V, current density 3.6 mA/cm², and brightness 105 cd/m³. Power conversion efficiency 1.3 It was 1 m/W.

[0089] To the formation Sumitomo 3M make of a protection closure layer, and tradename:FURORINATO FC-48,100ml the amorphous copolymer powder (the Du Pont make --) of a tetrafluoroethylene, and perfluoro -2, the 2-dimethyl -1 and 3-JIOKI SOL Tradename: The solution in which Teflon AFNo.1600 50g was dissolved was put into the glow box which circulated nitrogen gas, and after making into fine particles with a mortar 1g (Wako Pure Chem make) of activated carbon which supported 5 % of the weight of platinum, in addition, stirring distribution was carried out. Next, this solution was applied to the above-mentioned structure, the cast film was produced, and it considered as the protection closure layer (10 microns of thickness).

[0090] After adding 1g of 0.1 % of the weight support activated carbon of palladium and infiltrating it into the solution which melted [example 5] isooctane 0.01g to ether 5ml, After drying 100 degrees C for 30 minutes by the firing furnace which circulated nitrogen gas and making it fine particles with a mortar, the inside of the glow box which circulated nitrogen gas -- the Du Pont make -- Teflon AFNo.1600 and the Sumitomo 3M make in which 50g was dissolved -- in addition to FURORINATO FC-43 and 140ml of solutions, stirring distribution was carried out Next, it applied to the structure which used this solution in the example 4, the cast film was produced, and it considered as the protection closure layer (0.2mm of thickness).

[0091] [example 6] Sumitomo 3M make and tradename:FURORINATO FC-43,100ml -- the Du Pont make -- Teflon AFNo.1600 and the solution in which 50g was dissolved were made to distribute 0.5g of powder of 1 cobalt oxide (II) by the same method as an example 4, it applied to the structure which used this solution in the example 4, the cast film was produced, and it considered as the protection closure layer (0.5mm of thickness)

[0092] After having dissolved [example 7] oxalic acid vanadium 0.1g in 10ml of distilled water, adding and stirring 10g (the Wako Pure Chem make, tradename:WAKOGERU Q-50) of activated aluminas and making it harden by drying with an evaporating dish, it put into the electric furnace and heated at 600 degrees C in 2 hours. In addition to the paraffin (m. p.=42-44 degree C) heated at 50 degrees C, the obtained yellow powder was kneaded all over the glow box which circulated nitrogen gas. This solution was applied to the structure used in the example 4, was cooled radiationally, the thick film was produced, and it considered as the protection closure layer (about 1mm of thickness).

[0093] the [example 3 of comparison] Sumitomo 3M make -- the solution made to dissolve 50g (the Du Pont make, tradename:Teflon AFNo.1600) of amorphous copolymer powder of tetrapod follow ethylene, and perfluoro -2, the 2-dimethyl -1 and 3-JIOKI SOL in FURORINATO FC-43,100ml was put into the glow box which circulated nitrogen gas, it applied to the structure which used this solution in the example 4, the cast film was produced, and it considered as the protection closure layer (10

[0094] All over the glow box which circulated the [example 4 of comparison] nitrogen gas, the paraffin (m. p.=42-44 degree C) heated at 50 degrees C was applied to the structure used in the example 4, was cooled radiationally, the thick film was produced, and it considered as the protection closure layer (about 1mm of thickness). All over the glow box in which the organic EL element of examples 4-7 and the examples 3-4 of comparison circulated nitrogen gas, it is initial brightness 100 cd/m². The constant-current continuation drive and the unsteady drive in every month were performed.

----- Run * * * * The unsteady drive in every month ----- (Preservation life) A
reduction-by-half life A destructive life ----- Example 4 4,500 hours 20,000 hours or more Change[12
months after]-less example 5 5,000 hours 20,000 hours or more Change[12 months after]-less example 6 4,000 hours 20,000
hours or more Change[12 months after]-less example 7 8,000 hours 10,000 hours or more Example 3 of a change[12 months
after]-less comparison 150 hours 2,000 hours or more One month after The example 4 of dark-spot generating comparison 150

hours 1,000 hours or more One month after Dark-spot generating The effect was seen by extension of a reduction-by-half life, a destructive life, and a preservation life -----, thus by making a deoxidant etc. contain in it rather than it only attached a protection closure layer.

[0095] [Example 8]

The glass substrate with a transparent electrode (the Matsuzaki vacuum company make) which formed the 1000Å ITO (indium oxide-tin oxide) film in the production substrate glass of the structure of an organic EL element was cleaned ultrasonically in the acetone, and, subsequently boiling processing was carried out in ethanol. Furthermore, plasma treatment of air composition was carried out. This glass substrate with a transparent electrode that carried out surface treatment is set in vacuum devices, and they are N and N'-diphenyl at the degree of vacuum of 5×10^{-6} torr. - N, N' - (3-methylphenyl) 200Å vacuum evaporation of -1, the 1'-biphenyl -4, and the 4'-diamine (it is called Following TPD) is carried out. 100Å (inclination structured division) of portions in which the component of TPD and the aluminum complex (it is called the following Alq3) of 8-oxyquinoline has succeedingly the concentration gradient which changes continuously is formed, and it is Alq3 succeedingly. 200Å was deposited. Furthermore, 200nm vapor codeposition of magnesium (Mg) and the silver (Ag) was carried out by the atomic ratio of 10:1, and the structure of an organic EL element was produced.

[0096] the inside of formation of a protective layer, next Sumitomo 3M FURORINATO FC-72 -- the Du Pont make -- Teflon AFNo.1600 and the magnesium dust were distributed by ratio which is set to 100:1 by the weight ratio, and this was calmly applied on the structure obtained using the syringe, it waited to get dry, the operation same several times was repeated, and the protective layer was formed All the above operations were performed in nitrogen-gas-atmosphere mind. Thus, since the created organic EL element is a perfect solid-state component, it is easy to deal with it, and it does not have worries about a liquid spill. Moreover, it learned having left this element in a room temperature and air by experience, and after half a year, when direct current voltage was applied, light was emitted uniformly and a defect was not produced for an element.

[0097] Except not adding a magnesium dust to the protective layer of the element of the [example 5 of comparison] example 8, the element was produced by the completely same operation, and when the element left in air was made to emit light, many defects in which the size which is visible on the surface of an element in one month also with the naked eye was black arose.

[0098] The element was similarly produced except having replaced with molecular-sieve 4A (made in Kazumitsu Hiroshima) the magnesium as a dehydrating agent used in the [example 9] example 8. Consequently, a defect did not arise for an element for four months.

[0099] The element was similarly produced except having replaced with sulfuric-anhydride magnesium (made in Kazumitsu Hiroshima) the magnesium as a dehydrating agent used in the [example 10] example 8. Consequently, a defect did not arise for an element for three months.

----- A dehydrating agent Performance * ----- Mg With no defect for six months

Example 8 Molecular-sieve 4A With no defect for four months Example 9 Anhydrous MgSO₄ With no defect for three months

Example 10 Nothing It is defective generation in one month. The state of the luminescence side which is example of comparison 5----- when a performance impresses direct-current-voltage 10V was observed.

[0100] [Example 11]

What produced ITO by the thickness of 10nm by the vacuum deposition on the production 25mmx75mmx1.1mm [of the structure of an organic EL element] glass substrate was used as the transparent support substrate. This transparent support substrate was performed in isopropyl alcohol, ultrasonic cleaning was performed for 5 minutes in pure water after washing during 5 minutes, and UV ozone washing was further performed for 5 minutes. SAMUKO, Inc. international lab equipment was used for this UV ozone washing. This transparent support substrate is fixed to the substrate electrode holder of commercial vacuum evaporationo equipment (Japanese vacuum-technology company make). They are N and an N'-screw (3-methylphenyl) to the resistance heating boat made from molybdenum. - N, N'-diphenyl [1 and 1'-biphenyl]-4, and 200mg (TPD) of 4'-diamines are put in. Moreover, 200mg (DPVBi) of 4 and 4'-screw (2 and 2'-diphenyl vinyl) biphenyls was put into the different boat made from molybdenum, and the vacuum tub was decompressed up to 1×10^{-4} Pa. Then, the above-mentioned boat containing TPD was heated to 215-220 degrees C, the vacuum evaporationo of the TPD was carried out on the transparent support substrate by the 0.1-0.3nm [second] evaporation rate, and the hole-injection layer of 60nm of thickness was formed. The substrate temperature at this time was a room temperature. 40nm laminating deposition was carried out from another boat on the hole-injection layer, having used DPVBi as the luminous layer, without taking this out from a vacuum tub. The boat temperature of vacuum evaporationo conditions was 240 degrees C, the evaporation rate was 0.1-0.3nm/second, and substrate temperature was a room temperature. This was taken out from the vacuum tub, the mask made from a stainless steel was installed on the above-mentioned luminous layer, and it fixed to the substrate electrode holder again. Next, 200mg (Alq3) of tris (eight quinolinol) aluminum was put into the boat made from molybdenum, and the vacuum tub was equipped. Furthermore, 1g of magnesium ribbons was put into the resistance heating boat made from molybdenum, and into the different basket made from a tungsten, 500mg of silver wires was put in and they were deposited. Then, it is Alq3 after decompressing a vacuum tub up to 1×10^{-4} Pa. The boat into which it went is heated to 230 degrees C, and it is Alq3. 20nm was deposited by the 0.01-0.03nm [second] evaporation rate. Furthermore, it was begun simultaneously to carry out the vacuum evaporationo of the magnesium for silver from another molybdenum boat by the resistance heating method by the 0.01nm [second] evaporation rate at a 1.4nm [second] evaporation rate. The laminating vacuum evaporationo of the mixed metal electrode of magnesium and silver was carried out by the thickness of 150nm on the luminous layer by the above-mentioned conditions, and it considered as the counterelectrode. It aged by impressing the structure of this element by a unit of in 5 seconds at 0.5V interval in dryness nitrogen from 0V to 10V and 0V to -10V.

[00101] The silica glass (catalyst Chemicals company make) of 1 micrometer of mean particle diameters was mixed by 70% of the weight of the ratio as formation of a closure layer, next a closure layer to light hardening type adhesives (tradename ARON by the Toagosei chemical-industry company] tight VL). Were dropped so that the organic multilayer section and the electrode of the structure of the above-mentioned production of this closure layer might be covered, and it was made to harden by sunlight, and the closure layer with a thickness of 1mm was formed. [of an element]

[0102] The structure of an element was produced at the same composition as the [example 6 of comparison] example 11, and the process. The closure layer was formed on the same conditions as an example 11 on the structure, using the Toagosei chemical-industry company make and tradename ARON tight VL as a closure layer. When it produced at a time 50 elements which the example 11 and the example 6 of comparison closed, respectively, in the example 11, the number of the elements which having not had short-circuit by closure and stopped having luminescent ability at all by mechanical destruction was 40 in five pieces and the example 6 of comparison. Moreover, it installed at a time ten elements which the example 11 and the example 6 of comparison closed in durability test equipment (SH[by the TABAE id peck company]- 220), respectively, and the heat cycle durability test which repeats the heat cycle to which 25 degrees C -> 60 degrees C change [temperature] 60 degrees C -> 25 degrees C for 30 minutes for 30 minutes 10 times was performed. Consequently, there was an element which stopped having luminescent ability at all in two pieces and seven examples 6 of comparison by the example 11. The improvement of endurance in as opposed to [compared with the example 6 of comparison] improvement in the yield at the time of production and a heat cycle in an example 11 was clearly found from the two above-mentioned test results.

[0103] [Example 12]

The glass substrate with a transparent electrode (JIOMA tick company make) which formed the 1000A ITO (indium oxide-tin oxide) film in the production substrate glass of the structure of an organic EL element was cleaned ultrasonically in the acetone, and, subsequently it washed in UV washing station (UV[by the SAMUKO, Inc. international lab company]- 300). This glass substrate with a transparent electrode that carried out surface treatment is set in vacuum devices, 600A vacuum evaporation of N, N'-(3-methylphenyl)-1, the 1'-biphenyl -4, and the 4'-diamine (TPD) is carried out with the degree of vacuum of 5×10^{-5} torr, and it is the 8-hydroxy quinolinol aluminum complex Alq3 succeeding. 500A was deposited. Furthermore, 2000A vapor codeposition of magnesium (Mg) and the silver (Ag) was carried out by the atomic ratio of 10:1, and the structure of an organic EL element was produced.

[0104] **** of a layered product -- the Asahi Chemical Industry Co., Ltd. make and tradename: Saran Wrap (the oxygen transmission coefficient of Saran Wrap is 5.3×10^{-13} cc-cm/cm² and s- (cmHg)) were put for the structure of this element on the structure of this element in the vacuum (10 to 4 or less torrs), and the heat press (180 degrees C, 10 seconds) of the portion of the edge of the structure of an element was carried out. It is the element produced as mentioned above under the following evaluation conditions. The initial brightness of 100 cd/m². The constant-current drive was carried out.

[0105] It is initial brightness 100 cd/m², without forming a layered product for the structure used in the [example 7 of comparison] example 12 on it. The continuation drive was carried out under the evaluation conditions following by constant-current drive. the luminescence area after a both 500-hour drive [continuation] and in an element -- the case of an example 12 -- 3.95cm² receiving -- the case of the example 7 of comparison -- 2cm² it was. Evaluation conditions were driven in 25-degree-C dry air (1:4 mixture of gas of oxygen of 99.99% or more of purity, and nitrogen) (inside of a glasscase). Consequently, as shown in an example 12, the effect which suppresses generating of the field non-emitted light by closing was seen.

[0106]

[Effect of the Invention] it explained above -- as -- first [of this invention] - according to the third and fifth invention, degradation of the luminescence property by oxygen or moisture is prevented, it can continue at a long period of time, a stable luminescence property can be maintained, and a long lasting organic EL element can be offered. Moreover, according to invention of the fourth of this invention, mechanical degradation of the element by the temperature cycle can be prevented, it can continue at a long period of time, a stable luminescence property can be maintained, and a long lasting organic EL element can be offered. Furthermore, by combining the first - the fifth invention suitably, degradation of the element by oxygen, moisture, the temperature cycle, etc. can be prevented, and the long lasting organic EL element which was further excellent in quality can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the cross section showing the example of invention of the first of this invention typically.

[Drawing 2] It is the cross section showing the example of invention of the second of this invention typically.

[Drawing 3] It is the cross section showing the example of invention of the third of this invention typically.

[Drawing 4] It is the cross section showing the example of invention of the fourth of this invention typically.

[Drawing 5] It is the cross section showing the example of invention of the fifth of this invention typically.

[Drawing 6] It is the cross section showing typically other examples of invention of the fifth of this invention.

[Drawing 7] It is the cross section showing typically other examples of invention of the fifth of this invention.


[Description of Notations]


1 -- Structure

10 -- Organic EL element

11 -- Substrate

12 -- Anode plate

13 -- Cathode 

14 -- Organic luminescent material 

2 -- Layered product

2' -- Protection closure layer


21 -- An oxidation transmission coefficient is the organic layer of 1×10^{-12} cc-cm/cm² and s- (cmHg).

3 -- Protective layer

31 -- Dehydrating agent

4 -- Encapsulant

41 -- Oxygen-uptake layer

42 -- Oxygen barrier layer 

43 -- Light or thermosetting resin layer

44 -- Inorganic composition

5 -- Frame (glass or product made of a resin)

6 -- Glue line

7 -- Closure substrate

8 -- Solid-state case

[Translation done.]

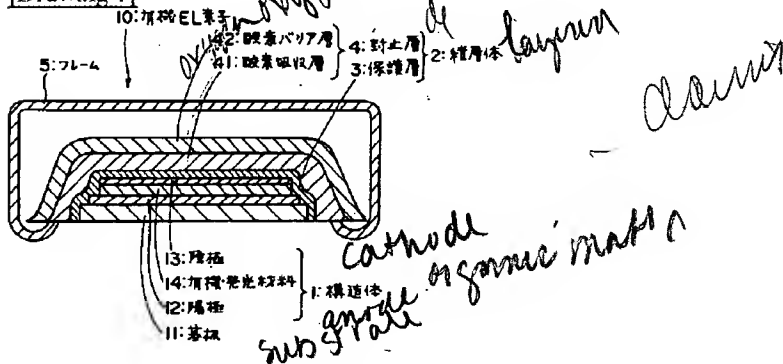
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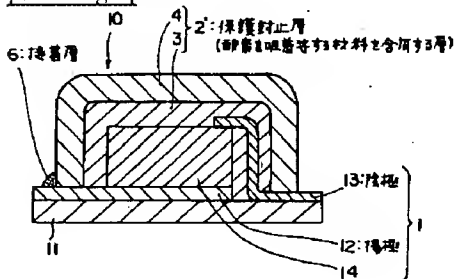
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DRAWINGS

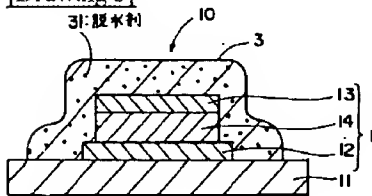
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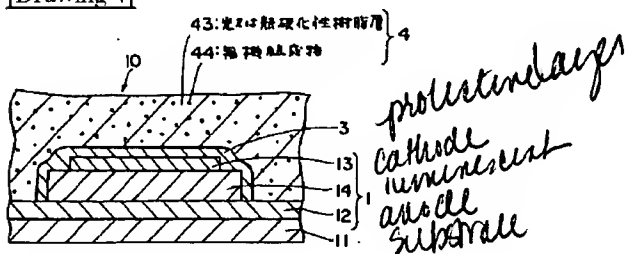
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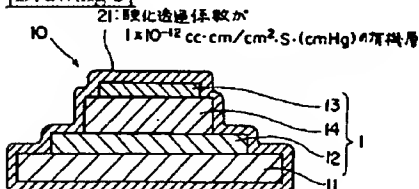
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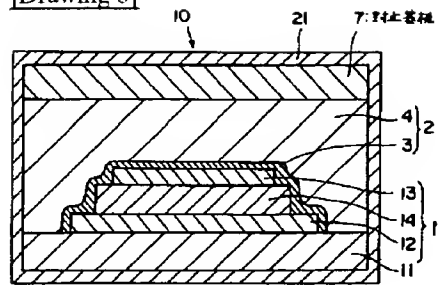
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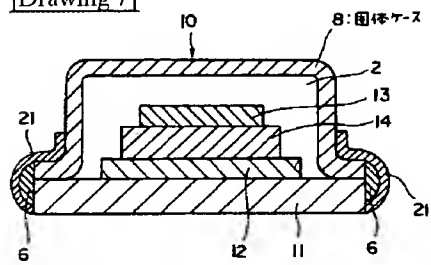
[Drawing 5]



[Drawing 6]



[Drawing 7]



[Translation done.]